CHEM 2430 – Organic Chemistry I – Fall 2015

Instructor: Paul Bracher

Quiz #4

Due: Monday, November 9th, 2015

1:10 p.m. (in class)

Student Name (Printed)	Solutions
Student Signature	N/A

Instructions & Scoring

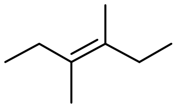
- Please write your answers on the official answer sheet. No answers marked in this booklet will be graded. Submissions submitted electronically will not be graded.
- You may use any resources you wish and collaborate with others.
- Any questions should be posted to the Blackboard discussion board so all students have equal access to the information.
- Your quiz answer sheet may be photocopied.

Problem	Points Earned	Points Available
I		30
II		18
III		18
IV		16
V		18
TOTAL		100

Questions, Required Information, Supplementary Information

Problem I. Multiple choice (30 points total; +5 points for a correct answer, +2 points for an answer intentionally left blank, and 0 points for an incorrect answer). For each question, select the best answer of the choices given. Write the answer, legibly, in the space provided on the answer sheet.

(1) E Which of the following statements is not true regarding compound **A**?

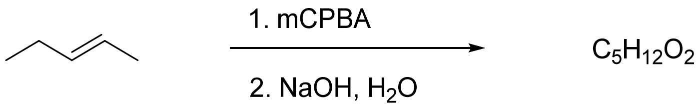


A

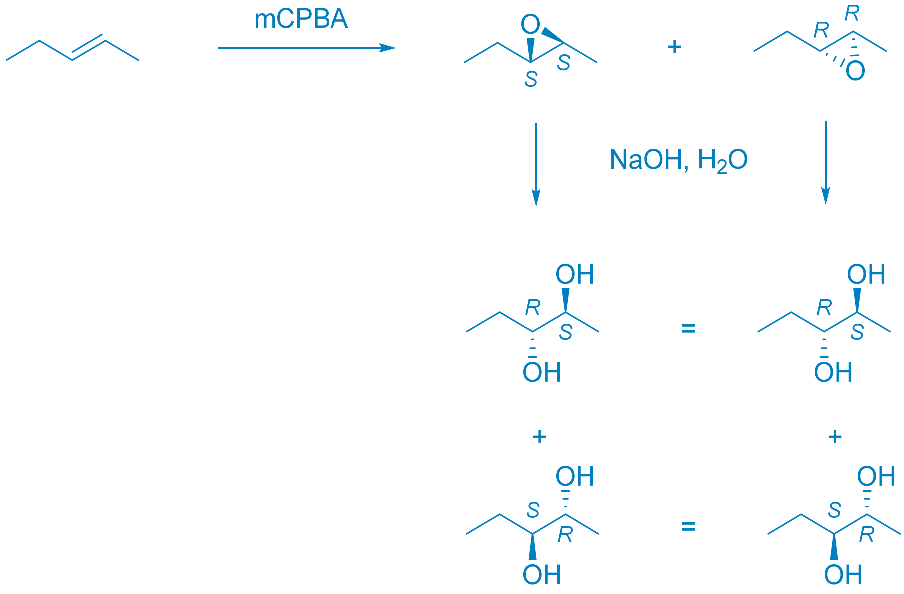
(a) compound **A** has poor solubility in water
(b) compound **A** is an *E*-alkene
(c) addition of Br_2 to the π bond of **A** will proceed through a chiral bromonium intermediate
(d) compound **A** will have a slower rate of hydrogenation on Pd-C than 3-hexene
(e) the heat of hydrogenation of **A** will be more negative than for 3-ethyl-3-hexene

(2) B

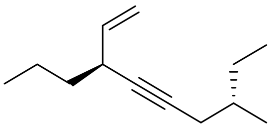
How many different compounds (stereoisomers) of molecular formula $C_5H_{12}O_2$ are produced by the following sequence?



(a) one
(b) two
(c) three
(d) four
(e) eight



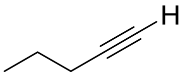
(3) ___D___ Which of the following is the best systematic name for compound **B**?



B

(a) (3*S*,7*S*)-7-vinyl-3-methyl-5-decyne
(b) (4*S*,8*S*)-4-vinyl-8-methyl-5-decyne
(c) (3*S*,7*S*)-3-methyl-7-propyl-8-nonen-5-yne
(d) (3*S*,7*S*)-7-methyl-3-propyl-1-nonen-4-yne
(e) (3*R*,7*S*)-3-methyl-7-propyl-8-nonen-5-yne

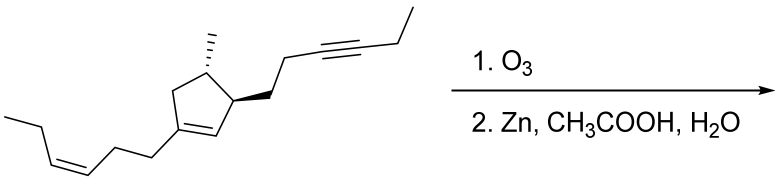
(4) ___B___ Which of the following statements is <u>not</u> true regarding compound **C**?

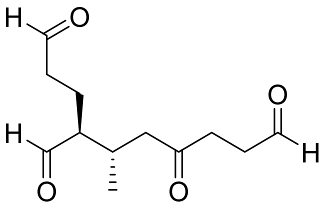


C

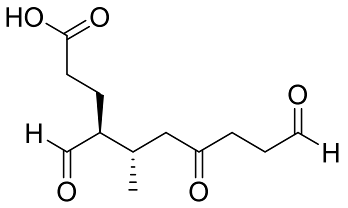
(a) compound **C** has a pK_a < 30
(b) addition of H_2 to **C** with the Lindlar catalyst yields a *cis*-alkene
(c) treatment of **C** with 1. 9-BBN, 2. H_2O_2, NaOH yields an aldehyde
(d) treatment of **C** with $HgSO_4$, H_2SO_4, H_2O yields a ketone
(e) compound **C** is a structural isomer of cyclopentene

(5) D Which of the following compounds is a product of this ozonolysis reaction?

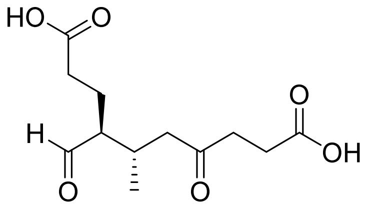




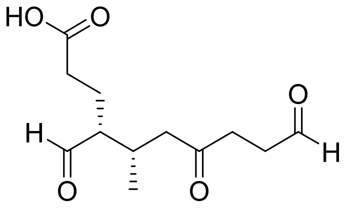
(a)



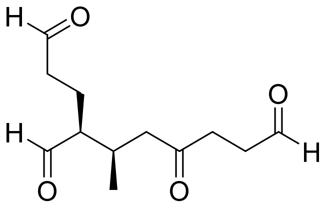
(b)



(c)



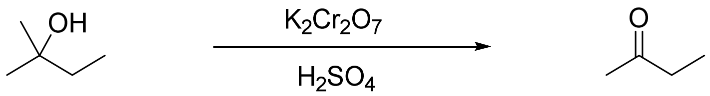
(d)



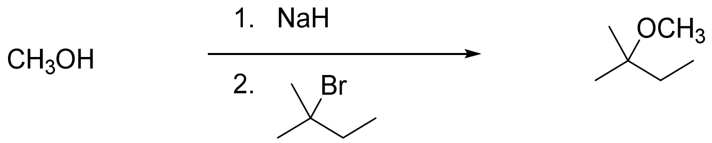
(e)

(6) C ____________ Which of the following reactions is <u>not</u> significantly flawed and will proceed as drawn?

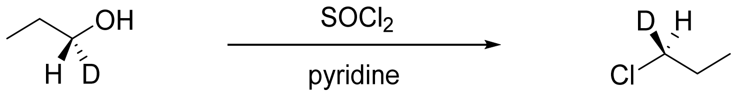
(a)



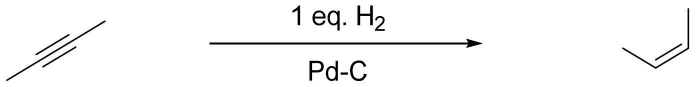
(b)



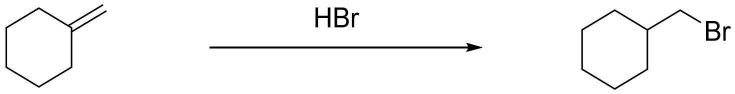
(c)



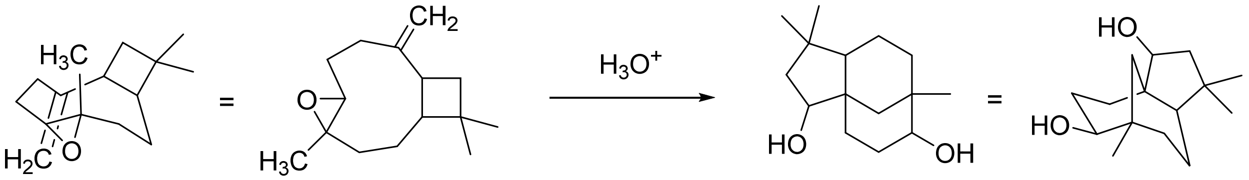
(d)



(e)

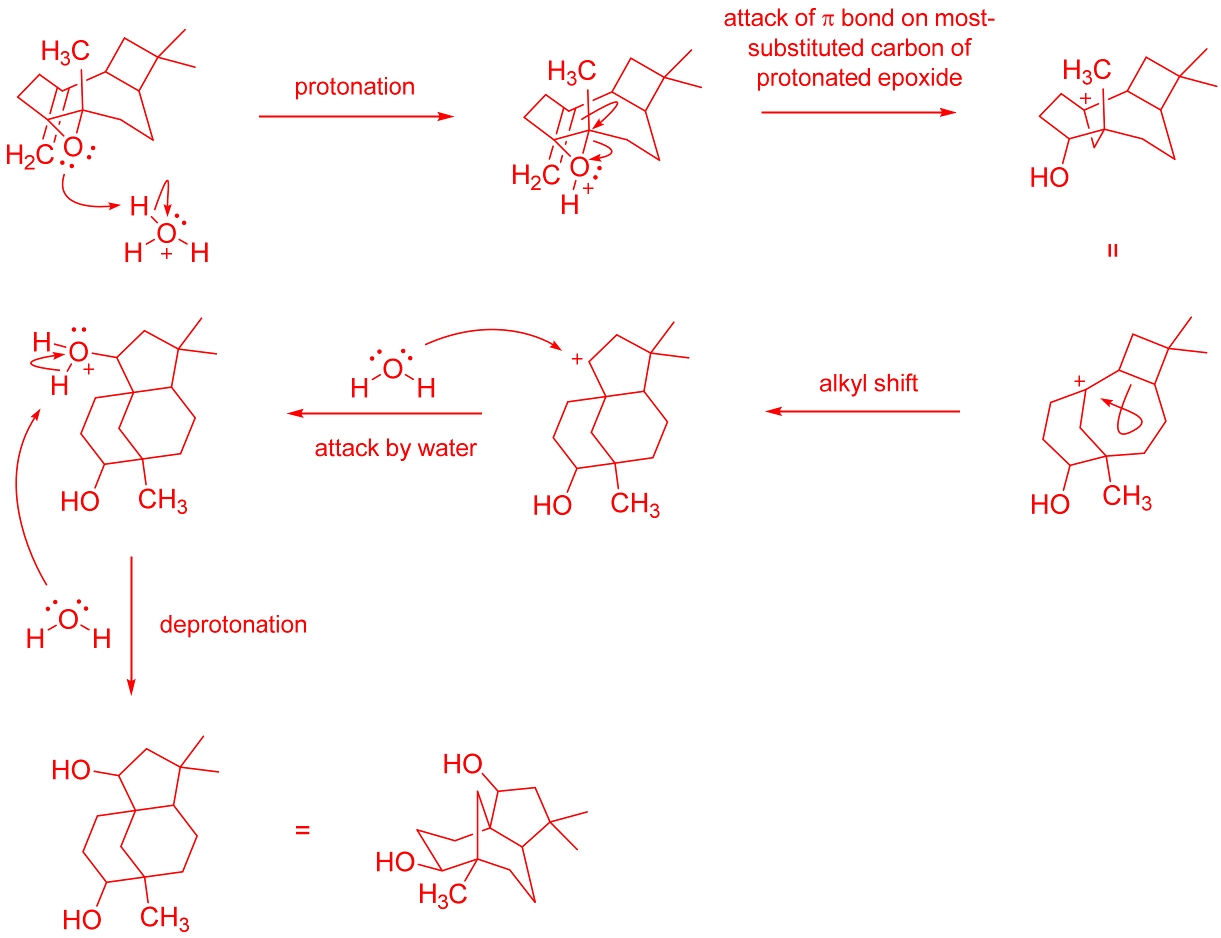


Problem II. Mechanism (18 points). Draw a sensible mechanism for the formation of **E** from **D** in aqueous, acidic solution. Remember to use proper "curved arrow notation" to account for the redistribution of electrons in the making and breaking of bonds. Show all intermediates in the reaction and any significant resonance forms that account for the stability of these intermediates. You may use whatever graphical renderings (2-D or 3-D, below) are most convenient for you. Do not worry about accounting for stereochemistry.



D **E**

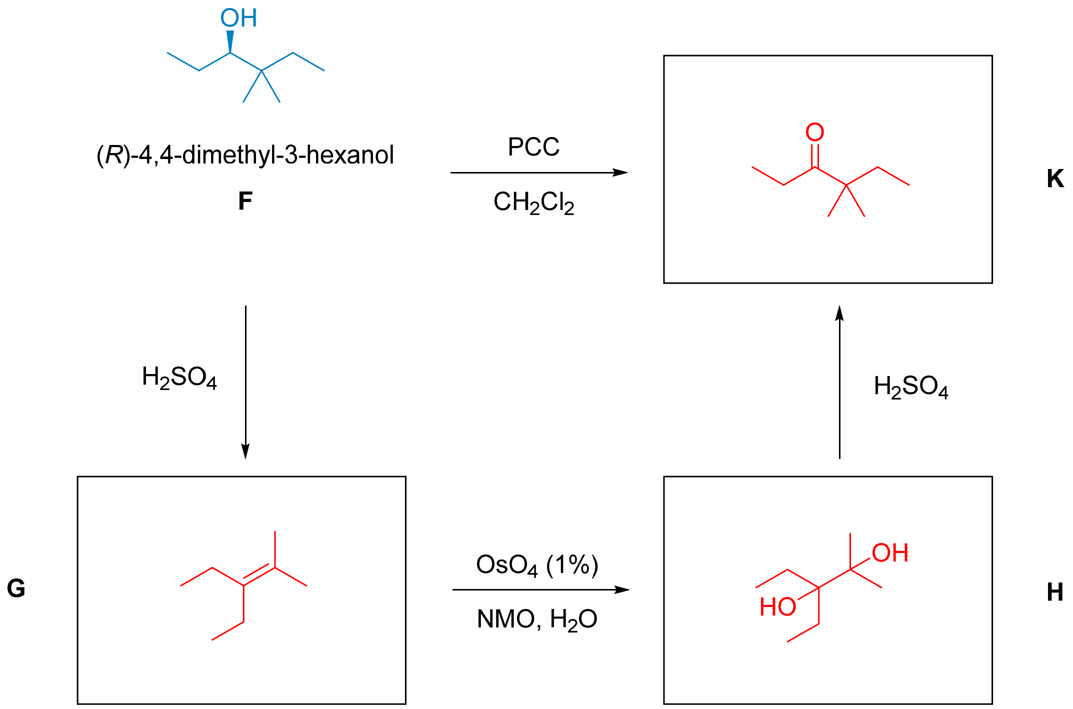
DOI: 10.1039/JR9530003124

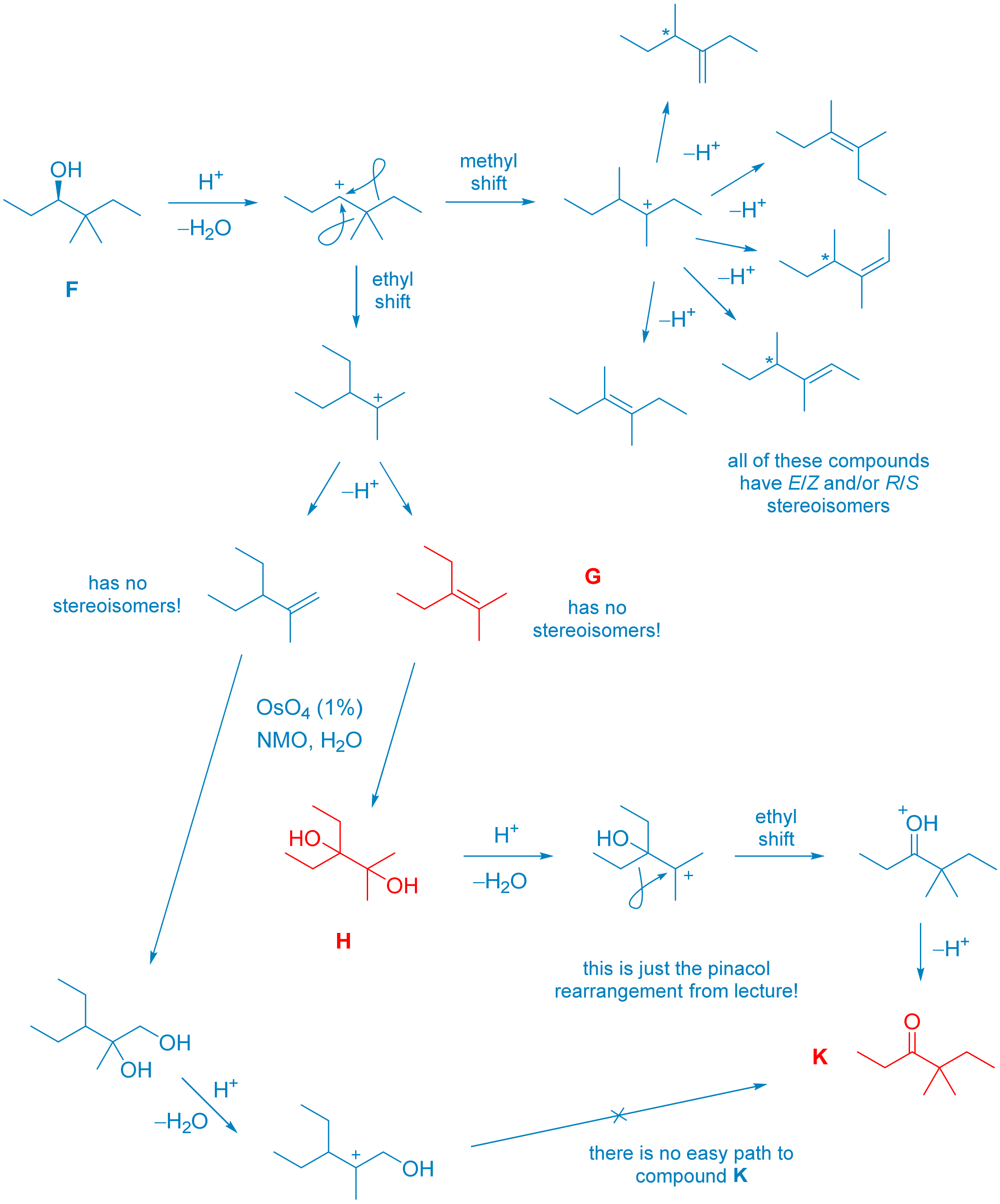


While the overall transformation might seem complex or intimidating, note how straightforward each individual step is—and there are only five steps total!

Problem III. (18 points) Roadmap Problem. Provide structures for compounds **G**, **H**, and **K** given the information listed below.

When (*R*)-4,4-dimethyl-3-hexanol (**F**) is treated with catalytic sulfuric acid, it produces compound **G**, an alkene with no stereoisomer. Treatment of **G** with catalytic osmium tetroxide and 1 equivalent of *N*-methylmorpholine *N*-oxide (NMO) yields compound **H**. Treatment of **H** with catalytic sulfuric acid affords a measurable quantity of compound **K**, which happens to be the same product that forms from the oxidation of **F** with pyridinium chlorochromate in dichloromethane.





all of these compounds have *E*/*Z* and/or *R*/*S* stereoisomers

has no stereoisomers!

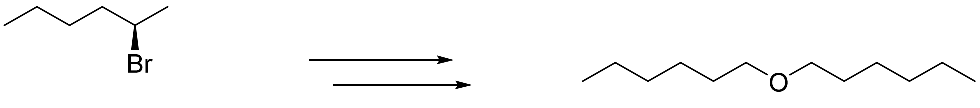
has no stereoisomers!

this is just the pinacol rearrangement from lecture!

there is no easy path to compound **K**

It is interesting to note that ethyl groups have a higher relative migratory aptitude than methyl groups.

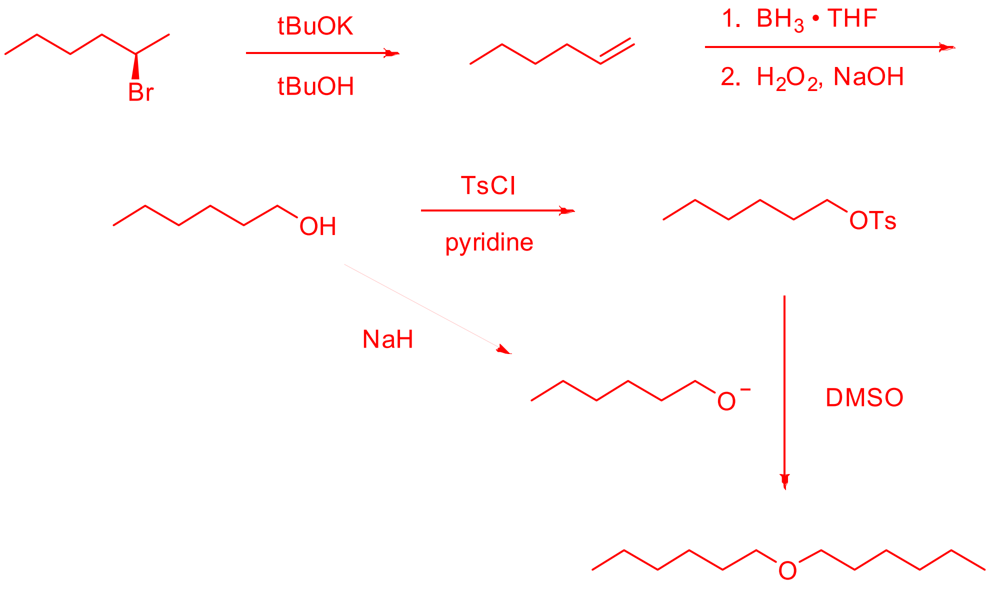
Problem IV. Synthesis (16 points). Outline a synthesis—i.e, a sequence of reactions—to prepare compound **M** using compound **L** as your only source of carbon atoms in the target. You may use any reagents and starting materials you wish.



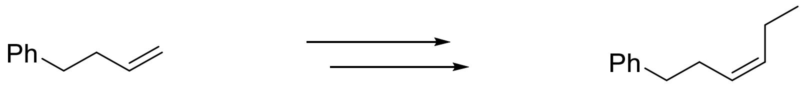
as your only source of carbon atoms in the product

L

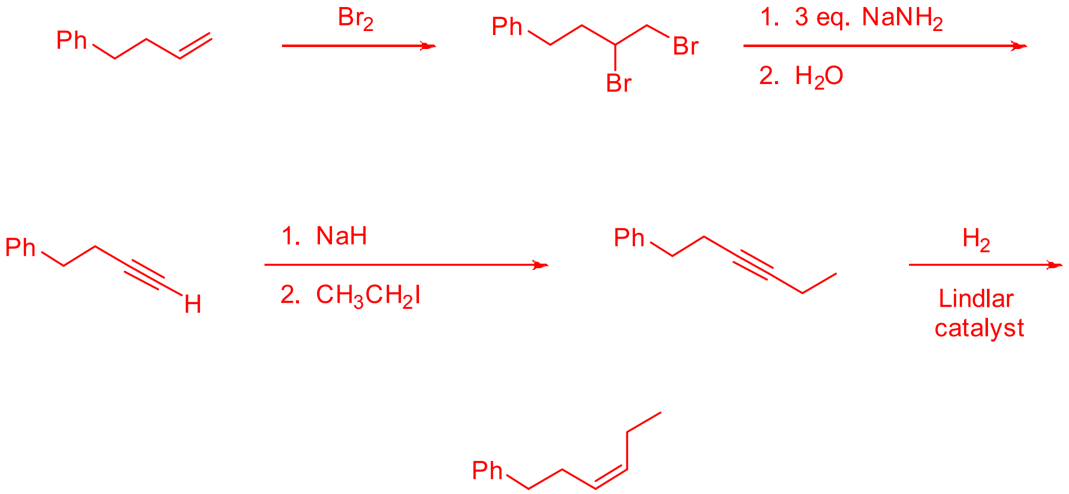
M



Problem V. Synthesis (18 points). Outline a synthesis—i.e, a sequence of reactions—to prepare compound **P** from compound **N** using any other reagents and starting materials you wish.



N **P**



The key difference to note between the starting material and target is that the carbon chain has been extended. The only versatile method we know so far (through chapter 12) to make carbon–carbon bonds is the alkylation of acetylide anions.

The acetylide is made by deprotonating a terminal alkyne, which is made by brominating the alkene and eliminating two equivalents of HBr using a very strong base. You need the 3rd equivalent of NaNH$_2$ because NH$_2^-$ is a strong base and will deprotonate the terminal alkyne. If you only added two equivalents of NaNH$_2$, you would produce 50% of the deprotonated alkyne, leaving 50% of the vinyl bromide intermediate.

Also, note that you need to include both Lindlar catalyst and H$_2$ in the last step. The former is the catalyst; the latter is the stoichiometric reductant.